URANIUM REMOVAL FROM WATER BY NANOFILTRATION

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ABSTRACT

The five most important uranium species for the mobilisation of uranium in natural water, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2\ (HPO_4)_2^{2-}$ and UO_2^{2+} have been generated in different model waters. Their rejection was determined at six nanofiltration (NF) membranes, which represent a broad spectrum of commercially available NF membranes, and at two open reverse osmosis (RO) membranes. The uranium rejection at the NF membranes at various hydrochemical settings was between 95 and 98 % in most cases. The rejection of other water constituents (phosphate, bicarbonate and electrical conductivity) differed between 40 and 97 %. The two RO membranes rejected 98 to 99.5 % of uranium and 93 to 99.5 % of other water constituents.

INTRODUCTION

It can be assumed that uranium is transported in water in the U^{6+} oxidation state (mainly as uranyl, UO_2^{2+}), and is insoluble in the U^{4+} state (Romberger, 1984). An exception are anoxic waters below pH 4 where uranous (U^{4+}) fluoride complexes are soluble (Langmuir, 1978). Uranium is usually complexed in natural water. In oxidised water uranyl fluoride (UO_2F^+) and uranyl phosphate complexes ($UO_2\ [HPO_4]_2^{2-}$) are the predominant uranium species below pH 7.5. Below pH 5 the unbound uranyl ion (UO_2^{2+}) is also soluble (Figure 1). Above pH 7.5, the uranyl di- ($UO_2[CO_3]_2^{2-}$) and tri-carbonate ($UO_2[CO_3]_3^{4-}$) anion complexes are the principal species. If the water is practically free of phosphate, the uncharged uranyl carbonate complex ($UO_2CO_3^0$) is also important between pH 5 and 6.5 (Figure 2). Beside the inorganic compounds, uranyl is also known to form complexes with humic acid.

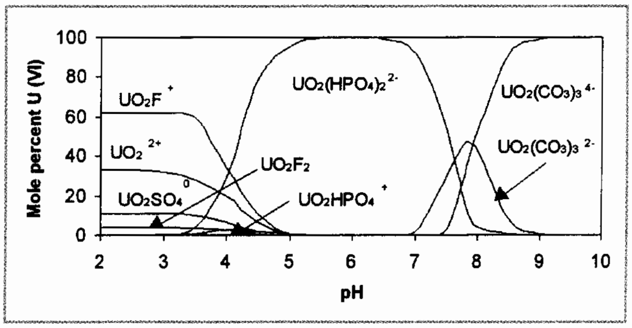

Figure 1. Distribution of uranyl complexes (U^{6+} species) for some typical ligand concentrations in oxidised groundwater at 25 °C: $P[CO_2] = 10\text{-}2.5$ atm, $\Sigma F = 0.3$ ppm, $\Sigma Cl = 10$ ppm, $\Sigma SO_4 = 100$ ppm, $\Sigma PO_4 = 0.1$ ppm, $\Sigma SiO_2 = 30$ ppm (after Langmuir, 1978).

Membrane technology is a proper method to remove dissolved compounds from water. Effective removal of uranium compounds is possible by membranes with very small pore sizes ("molecular sieves") only. This applies to the membrane processes reverse osmosis (RO) and nanofiltration (NF). Generally, RO shows higher rejection of water constituents than NF, but also has a lower flow velocity and a higher pressure requirement. Very high efficiencies of 95 to 99 % for uranium removal from water by RO has been reported by several authors (Huxstep and Sorg, 1987; Chu et al., 1990; Awadalla and Kumar, 1994; Huikuri et al., 1998).

In this study the most important uranium species for the mobilisation of uranium have been generated in different model waters and their rejection was determined at a broad spectrum of commercially available NF membranes. Aim of the study was to be able to predict the general usability of NF membranes to remove uranium from water.

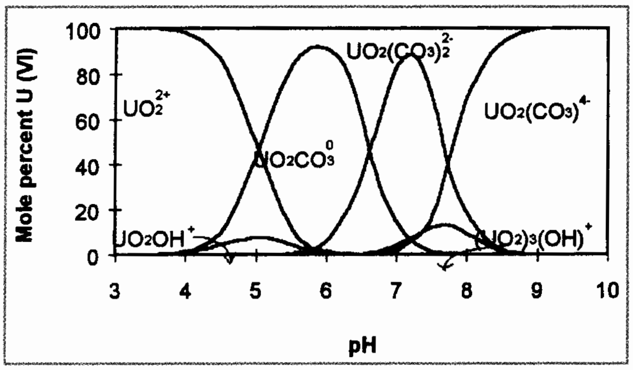

Figure 2. Distribution of uranyl complexes (U^{6+} species) in the oxidised system water, uranium, carbon dioxide for $P(CO_2) = 0.01$ bar and $\Sigma U = 10^{-8}$ M at 25 °C (after Langmuir, 1978).

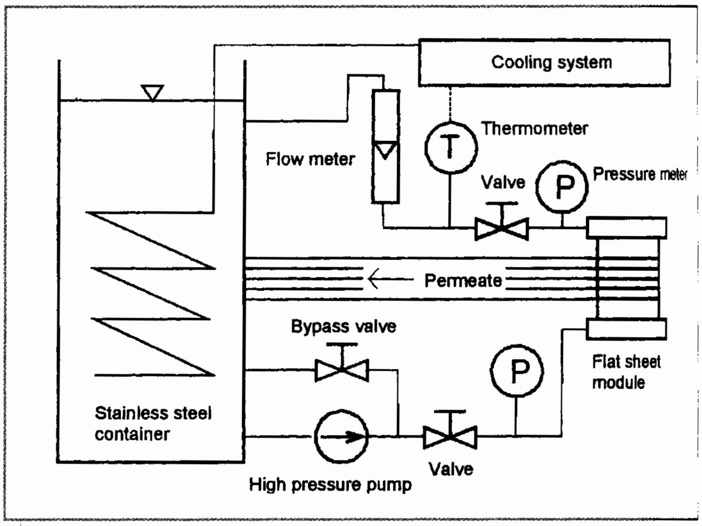

Figure 3. Scheme of the plate module membrane filtration pilot plant.

INVESTIGATION

To determine the suitability of different nanofiltration (NF) membranes for the removal of dissolved uranium from water, several experiments were carried out with a plate module membrane filtration pilot plant (Figure 3). Either five or eight flat sheet membranes were installed simultaneously in the plate module, each with a filtration area of 360 cm^2. The membranes were separated by plastic plates which kept a distance between the membrane sheets and led the permeate and the concentrate through the module. The influx water overflowed one membrane after the other, whereas the total recovery (permeate flux of all membranes related to the influx) was 2 %. Because of this low value the feed water concentration for all membranes was fairly the same and the concentration polarization at each membrane could be ignored.

The operation pressure was about 8 bar (8 to 8.5 bar in front of the module and about 7.5 bar behind the module). Six different NF membranes (companies in brackets), Desal 5 DK, Desal 5 DL, Desal 51 HL (all Osmonics Desal), NF 90, NF 45 (DOW) and Romaco (Romaco), and two open RO membranes, PVD 1 (Hydronautics) and Desal 3 SG (Osmonics Desal) were installed. Several artificial uranium solutions were used as experiment water (150 liter) with uranium contents of 1 or 10 mg/L. Using a high pressure pump, the water was pressed from a stainless steel container through the module and back into the container in circulation mode. With a valve and a bypass valve in front of the module the wanted throughput and pressure could be adjusted. By two pressure meters the trans-module pressure loss could be determined. The permeate of the membranes also flew back into the container, each through a single tube. From those tubes the permeate samples could be taken. By a flow meter at the end of the circulation a constant flow velocity of the concentrate was controlled for all experiments. Besides, a cooling system controlled a constant water temperature of 20 °C.

The model waters were prepared to generate the five most important uranium species occurring in natural water: $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ (system water / carbon dioxide / uranium), $UO_2(HPO_4)_2^{2-}$ (system water / phosphate / uranium) and the cation UO_2^{2+} (several systems below pH 5). By investigating those complexes, which represent anion, cation and uncharged uranium compounds, the general suitability of NF to remove uranium from water can be estimated.

Uranium was analysed by using ICP-MS, phosphate by photometry and bicarbonate by titration.

RESULTS

The specific permeate flux of the used membranes at a trans-membrane pressure of about 8 bar is shown in Table 1. The values range between 24 and 57 Lm^{-2}h^{-1}.

Membrane	51 HL	5 DK	5 DL	NF 90	NF 45	Romaco	PVD 1	3 SG
Specific flux, Lm^{-2}h^{-1}	57	27	37	52	33	28	27	24

Table 1: Specific permeate flux at a trans-membrane pressure of about 8 bar.

The rejection of uranium, bicarbonate and electrical conductivity at five NF membranes, dependent on the pH, using a carbonate model water without phsphate, is shown in Figure 4. The main water constituents are sodium (about 75 mg/L) and bicarbonate (3 mmol/L at pH 8.3, 2.8 mmol/L at pH 7.3 and 0.9 mmol/L at pH 5.9). The rejection of uranium is between 95 and 98 % in 12 cases, between 90 and 95 % in two cases and 81 % in one case. Bicarbonate and conductivity rejection are 50 to 95 % and 40 to 95 %, respectively.

The rejection of uranium, phosphate and electrical conductivity at all eight membranes (NF and RO), dependent on the pH value, using a phosphate model water without carbonate is shown in Figure 5. Because of the low phosphate concentration of the

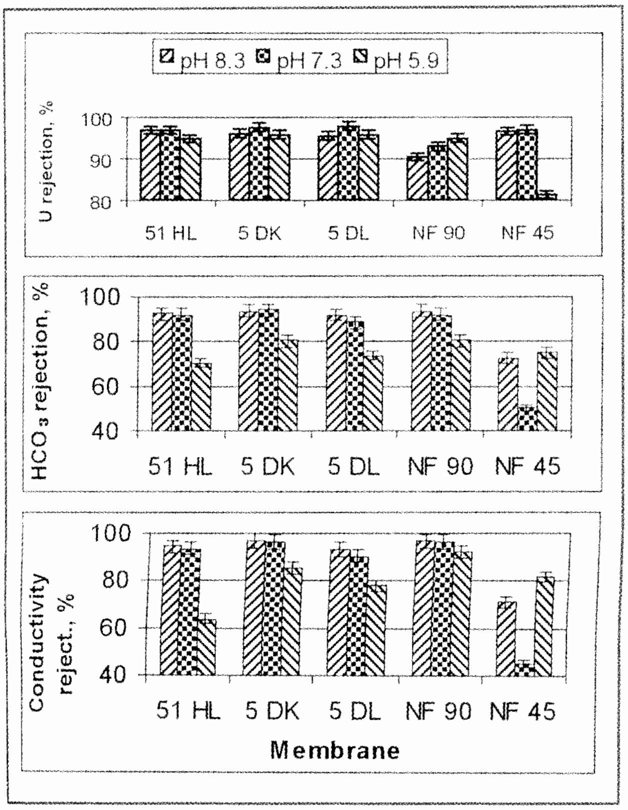

Figure 4. Rejection of uranium, bicarbonate and electrical conductivity at different membranes, dependent on the pH value in a carbonate model water without phosphate.

water (10 mg/L) the main water constituents are sodium and chlorine (NaCl concentration about 200 mg/L). The rejection of uranium is between 95 and 99 % in 18 cases, between 90 and 95 % in 11 cases and between 85 and 90 % in 3 cases. Phosphate and conductivity rejection are 40 to 99 % and 5 to 98 %, respectively.

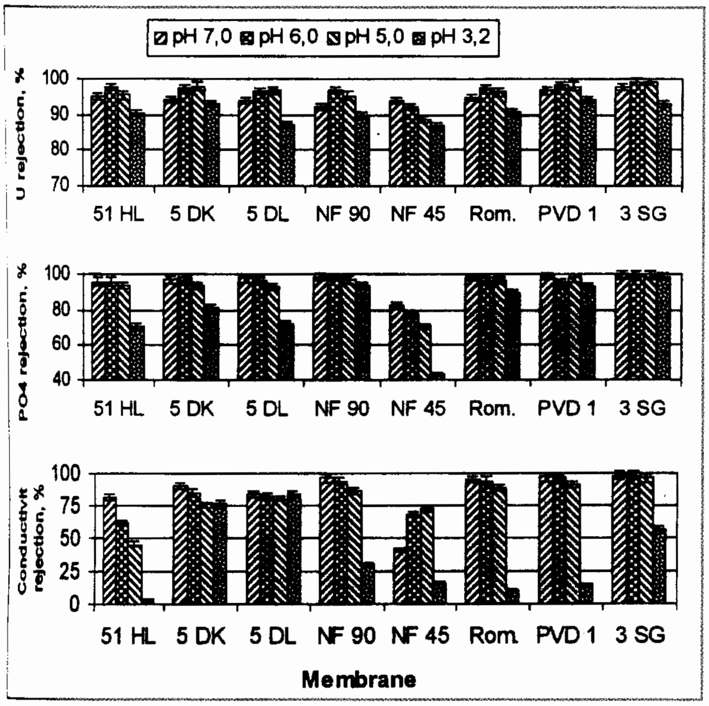

Figure 5. Rejection of uranium, phosphate and electrical conductivity at different membranes, dependent on the pH value in a phosphate model water without present carbonate.

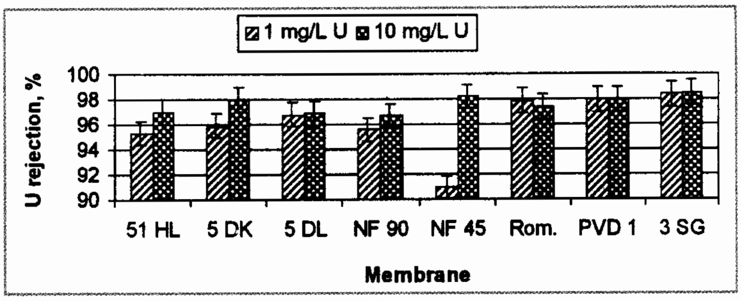

Figure 6. Rejection of uranium at different membranes, dependent on the uranium concentration.

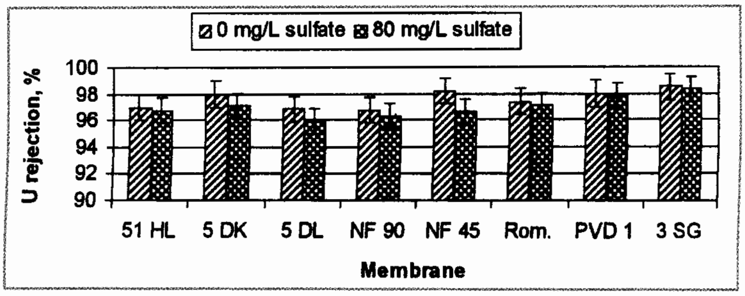

Figure 7. Rejection of uranium at different membranes, dependent on the sulphate concentration.

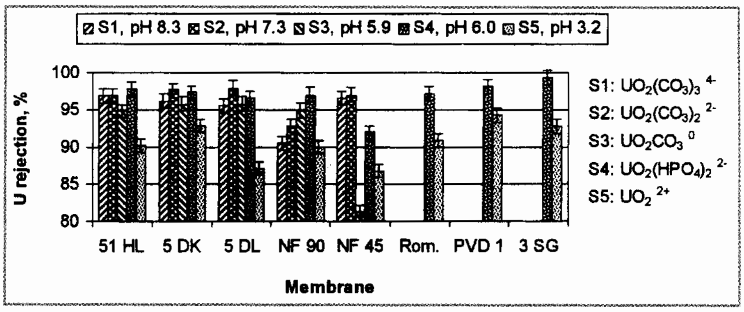

Figure 8. Rejection of the five most common uranium species (S1 to S5) in oxidised natural water at six NF and two open RO membranes.

The result of an experiment to determine the influence of the uranium concentration on the uranium rejection, using a NaCl / phosphate model water (pH 6.0, electrical conductivity 400 µS/cm, PO_4 concentration 10 mg/L), is shown in Figure 6. The differences of the uranium rejection for 1 and 10 mg/L (uranium concentration) are within 2 % in 7 cases. In one case the rejection is 7 % higher at the 10 mg/L concentration.

The result of an experiment to determine the influence of the sulfate concentration on the uranium rejection, using a NaCl / sulfate / phosphate model water (pH 6.0, electrical conductivity 600 µS/cm, PO_4 concentration 10 mg/L, SO_4 concentration about 80 mg/L), is shown in Figure 7. The differences for the uranium rejection with or without sulfate are below 2 % in all cases.

Finally, the main results of all experiments are summarised in Figure 8.

DISCUSSION

In natural water the uranyl carbonate complexes $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and, if phosphate is present, the uranyl phosphate complex $UO_2(HPO_4)_2^{2-}$ are mainly responsible for the mobility of uranium. Below pH 5, the pure uranyl cation UO_2^{2+} is also important. Those five uranium species have been generated in model waters and their rejection at six NF membranes and two open RO membranes was determined in several experiments.

The summarised results of all experiments (Figure 8) show that the uranium removal from water at the six tested NF membranes was mainly between 90 and 98 %. Especially the three divalent and multivalent uranyl anion complexes $UO_2(HPO_4)_2^{2-}$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ were mostly removed to 95 % or more. Those three complexes are the predominant uranium species in natural water above pH 4. The uncharged uranyl carbonate complex, $UO_2CO_3^0$, that predominates in phosphate free water between pH 5 and 6.5, was also removed to about 95 % in most cases. Besides, the rejection of the pure uranyl cation at pH 3.2 was between 87 and 93 %. The high rejection of those five uranium compounds is a first sign, that uranium can be removed from water by NF membranes quite effectively. This seems to be valid over a wide range of hydrochemical settings, even in very acidic waters.

The experiment with the extraordinary high uranium concentration of 10 mg/L has shown no major difference in the removal efficiencies of the membranes, compared to the 1 mg/L experiments. Therefore, clearly worse removal efficiencies are not to be expected during concentration processes at membranes, which will take place in the case of a higher recovery. Further, there seems to be no clear effect on the uranium removal efficiency due to the presence of a high number of competing ions in the water. This was shown by the experiments with high and low sulphate concentrations.

Comparing the rejection results of the NF membranes, it can be summarised that the three membranes 5 DK, 5 DL and Romaco, which are at the RO site of NF, show quite similar results: uranium rejection between 95 and 98 % and rejection of other water constituents (phosphate, bicarbonate and electrical conductivity) between 75 and 97 % (pH 5 to 8.3). The membrane NF 90, which is also more on the RO site of NF, rejects uranium slightly worse (91 to 97 %) and other water constituents slightly better (80 to 98 % at pH 5 to 8.3). The membrane 51 HL removed uranium also highly effective (95 to 98 %), but, since it is a little more open than the 4 membranes mentioned above, the rejection of other water constituents was only between 45 and 95 % (pH 5 to 8.3). The lowest rejection for both uranium and other water constituents took place at membrane NF 45, which is the most open NF membrane (of the tested ones). The uranium rejection at this membrane was between 81 and 98 % and the rejection of other water constituents between 40 and 80 % (pH 5 to 8.3).

Beside the six NF membranes two RO membranes were tested for comparison. Like it was to be expected, the membranes PVD 1 and 3 SG rejected both uranium (98 to 99.5 % at pH 5 to 8.3) and other water constituents (93 to 99.5 %) more effectively than the NF membranes.

Finally, an estimation on organic uranium species should be made, since several authors assume that a certain part of uranium mobilised in water might be due to organic compounds. It can be estimated that the rejection of organic uranium compounds would not be lower than the rejection of the investigated compounds. The reason is that any organic uranyl species, whether anionic, cationic or uncharged, surely would be bigger and heavier than the investigated inorganic uranyl compounds. The molecular weight of the investigated compounds, however, was the main factor for the quite high rejection at all membranes. This is indicated by the similarity of the results of the uranium removal efficiencies in all experiments, without depending on the charge of the compounds. And indeed, even the molecular weight of the lightest uranium compound, the pure uranyl cation, UO_2^{2+} (270 dalton), is already above the typical molecular weight cut-off (MWC: weight of uncharged organic molecules which are rejected practically completely) of NF membranes. The molecular weight of $UO_2(HPO_4)_2^{2-}$, for example, is 460 dalton. The typical MWC of NF membranes is about 250 dalton.

CONCLUSION

This study enables to estimate the suitability of NF membranes to remove uranium from water. It showed that the most important uranium species in natural water, which represent anion, cation and uncharged compounds, can be removed to about 95 % over a wide range of pH and hydrochemical settings. It showed further, that the heavy molecular weight of uranium compounds is mainly responsible for the high rejection. Since even the molecular weight of the uranyl cation, which is the lightest uranium compound in water, is above the typical molecular weight cut-off of NF membranes, it can be expected, that the rejection of other uranium compounds, not investigated in this study, would also be above 90 or 95 %.

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